

Effect of Fe(III) Species on the Stability of a Water-Model Oil Emulsion with an Anionic Sulfonate Surfactant as an Emulsifier

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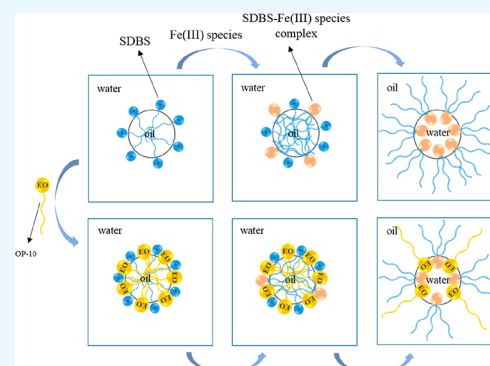
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ABSTRACT: The stability of an emulsion has an important effect on enhancing oil recovery. However, the effect of ions with different valences on the stability of the emulsion emulsified by an ionic surfactant is not fully understood. In this study, the effects of Fe(III) species on the stability, microscopic morphology of droplets, interfacial properties, and rheological properties of water-model oil emulsions emulsified by sodium dodecyl benzenesulfonate (SDBS) were explored. The effect of Fe(III) species on the stability of a W/O crude oil emulsion was also explored. The stability experiment results show that the addition of the Fe(III) species impairs the stability of the model oil-in-water (O/W) emulsion, in which the O/W model oil emulsion is inverted to a water-in-model oil (W/O) emulsion at ~ 99 ppm. With the increase of Fe(III) species concentration, stable W/O model oil and W/O crude oil emulsions are obtained. The rheological results indicated that the existence of the Fe(III) species has a remarkable effect on the viscosity and viscoelastic behaviors of the water-model oil emulsion. The calculation results based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory are in accord with the stability experiment results. Furthermore, the addition of EO groups makes the phase inversion point appear at a higher Fe(III) species concentration, forming a more stable W/O model oil emulsion and a more unstable O/W model oil emulsion. The experimental results are helpful to comprehensively understand the effect of Fe(III) species on the stability of an emulsion emulsified by an anionic sulfonate surfactant, which can help to enhance the oil recovery.



1. INTRODUCTION

In recent years, increasing oil production is crucial to deal with the global energy crisis. Only one-third of the crude oil in the reservoir can be exploited by conventional primary and secondary oil recovery methods.¹ A tertiary oil recovery procedure is proposed to further utilize the rest of the oil, in which stable emulsions are used to improve the sweep efficiency after water flooding.^{2–7} The addition of surfactants as emulsifiers makes emulsions more stable. The role of emulsifiers is to reduce the oil–water interfacial tension (IFT) and prevent droplets from coalescing with each other by forming a protective film on the oil–water interface.^{8–,11}

The type and concentration of ions in emulsions affect the adsorption of emulsifiers on the oil–water interface and then affect the stability of emulsions. Some studies have investigated the effect of ions on the stability of emulsions emulsified by different emulsifiers. Sun et al.¹² observed the effect of sodium ion (Na^+) concentration on the stability of W/O emulsions. They found that the water droplet size in a heavy oil emulsion increased with an increase in salinity, resulting in a decrease in the emulsion stability. Davis et al.¹³ found that the addition of Na^+ reduced the electrostatic repulsion force of the anionic surfactant and allowed the surfactant to accumulate more

closely on the oil–water interface, enhancing the stability of O/W emulsions stabilized by sodium lauryl ether sulfate. Compared with monovalent ions, divalent ions, such as calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}), have more significant effects on the emulsion stability, which may be attributed to the difference in the chemical structure and valence state.^{14–16} Kazemzadeh et al.¹⁷ pointed out that the interaction of asphaltene with Ca^{2+} and Mg^{2+} in the water phase caused a more stable water-in-crude oil emulsion, which resulted in droplets with a smaller average area and a lower value of interfacial tension.¹⁸ Previous studies have mainly been focused on the effects of monovalent and divalent cations on the stability of emulsions stabilized by different emulsifiers. However, there have been few studies on the effect of higher valence cations, especially the universal Fe(III) species (Fe^{3+} and its hydrolysates) in stratum water, on the emulsion

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stability. In addition, in recent years, with the extensive use of acid fracturing in the oilfield, the flowback acid oil is seriously emulsified and the demulsification is more difficult.¹⁹ This not only causes great trouble in the field treatment but also causes great economic losses to the oilfield enterprises. Compared with the conventionally produced fluid, the pH of the acid flowback fluid is lower, resulting in a larger amount of Fe(III) species due to the acid corrosion of metal pipes, which further improves the emulsification of the flowback fluid, leading to a more complex demulsification.^{19,20} Therefore, it is essential to study the effect of Fe(III) species on the emulsion stability.

Due to a lack of investigations on the effect of Fe(III) species on the stability of emulsions emulsified by an anionic surfactant, sodium dodecyl benzenesulfonate (SDBS), a common surfactant in oilfields, was used as an emulsifier in this work. The study investigates the effect of Fe(III) species on the stability of a water-model oil emulsion and water-crude oil emulsion. In addition, ethylene oxide (EO) groups can affect the adsorption of an anionic surfactant on the oil–water interface,²¹ and so the effect of octylphenol polyoxyethylene ether (OP-10), a polyether surfactant, with EO groups on the model oil emulsion stability in the presence of SDBS and Fe(III) species was studied. The water-model oil emulsion was prepared by using a kerosene solution containing 1 wt % crude oil-1 as oil phase (model oil) in order to make the properties of oil phase close to those of crude oil. Comprehensive evaluations of the emulsion stability were obtained by determinations of the macroscopic phase separation, microscopic morphology of droplets, interfacial properties, and rheological properties and by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. The experimental results show that Fe(III) species have a pronounced effect on the emulsion stability. These results provide insights into the effect of Fe(III) species on the stability of an emulsion emulsified by an anionic sulfonate surfactant and have a great significance for an enhancement of oil recovery.

2. RESULTS AND DISCUSSION

2.1. Emulsifying Properties of Sodium Dodecyl Benzenesulfonate (SDBS) as an Emulsifier for Water-Model Oil System. The concentration of the emulsifier affects the emulsifying property in an emulsion system. The emulsifying property of SDBS was examined by assessing the emulsification index (EI) of O/W emulsions. Figure 1 shows the EI of O/W emulsions with different SDBS concentrations

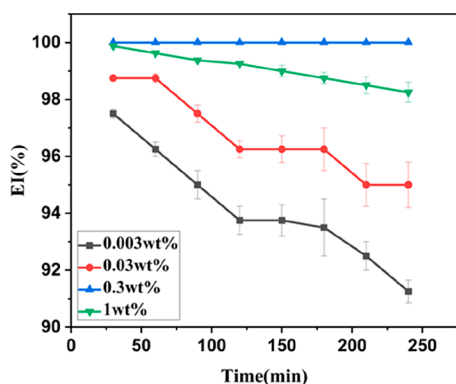


Figure 1. Effect of SDBS concentration on the emulsification properties. The solid lines are guides for the eye.

within 4 h. The general trend is that the EI decreases with an increase in SDBS concentration. The stability of an oil–water interfacial film is the key factor affecting the stability of emulsions. Xu et al.²² studied the effect of SDBS concentration on the stability of a crude oil–pure water interfacial film by molecular dynamics simulations (MD), indicating that the thickness of the interfacial film increases and the structure of the interfacial film is more stable with an increase in surfactant concentration. The formation of the stable interfacial film makes it difficult for oil droplets to aggregate, resulting in a decrease in the volume of water separation from the emulsion.²³ It is worth noting that the EI is smaller when the SDBS concentration increases from 0.3 to 1 wt % in the emulsions. When the SDBS concentration is higher (1 wt %), SDBS molecules on the interface may be solubilized in the bulk by a great number of SDBS aggregations, which weakens the strength of the interfacial film.^{24–27} Therefore, it is not true that the higher the concentration of the surfactant, the better the emulsifying property.

2.2. Effect of Fe(III) Species Concentration on the Model Oil Emulsion Stability. In order to get SDBS to have a better emulsifying effect, 0.3 wt % was used as the SDBS concentration throughout the following studies.

The relationships between the types of emulsions and Fe(III) species concentrations are shown in Figure 2a. In the absence of EO groups, O/W emulsions are formed when the Fe(III) species concentrations are from 0 to 83 ppm and W/O emulsions are formed when the Fe(III) species concentrations are from 99 to 166 ppm. However, the Fe(III) species concentration required by the system in the presence of EO groups to cause the emulsion phase inversion is higher than that required by the system in only the presence of SDBS.

As shown in Figure 2b, the EI of the O/W emulsion with and without EO groups decreases with an increase in Fe(III) species concentration. The result indicates that the stability of the emulsion decreases with an increase in Fe(III) species concentration. The reasons for this phenomenon can be explained by the lipophilicity variation of the surfactant in the presence of an electrolyte. The cation interacts with the polar headgroup of the anionic surfactant on the interface through an electrostatic interaction, and with an increase in ionic strength, this interaction will weaken the hydration degree of the polar headgroup and make the surfactant more lipophilic.^{28–30} Fe(III) species may interact with the polar headgroup of SDBS to form the more lipophilic SDBS–Fe(III) species complex.

In order to verify the formation of the SDBS–Fe(III) species complex and its lipophilicity, we obtained an SDBS–Fe(III) species complex by using a literature procedure.³¹ Adding the SDBS–Fe(III) species complex to the same volumes of kerosene and deionized water, respectively, we find that the SDBS–Fe(III) species complex is more soluble in kerosene, as shown in Figure S1, indicating that the SDBS–Fe(III) species complex is a more lipophilic surfactant.

The Bancroft rule holds that the high-solubility phase of the emulsifier is the continuous phase of the emulsion. Therefore, the formation of the lipophilic SDBS–Fe(III) species complex leads to an unstable O/W emulsion. Furthermore, ζ potentials of the system without Fe(III) species are -96.24 and -69.88 mV in the absence and presence of EO groups, respectively, as shown in Figure 3a. However, the absolute value of the ζ potential decreases with increasing Fe(III) species concentration before reaching the phase inversion point, which

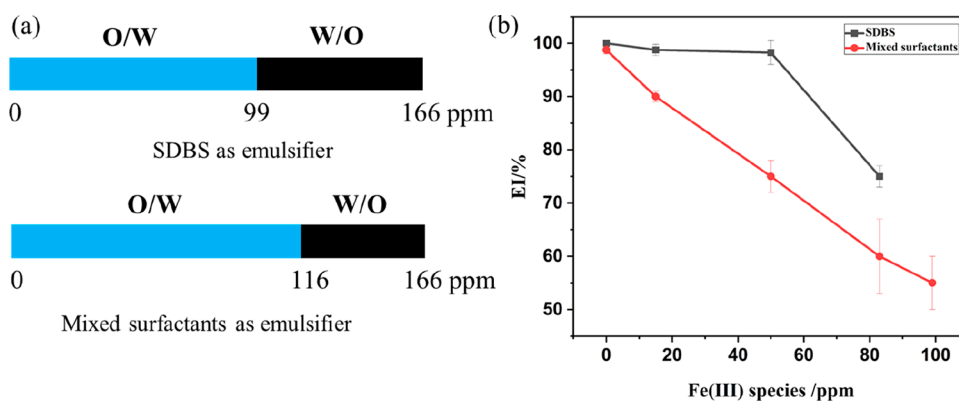


Figure 2. (a) Relationship between the types of emulsions and Fe(III) species concentration (ppm). (b) Emulsification indexes (EIs) of the O/W emulsions with an increase in Fe(III) species concentration. The solid lines are guides for the eye.

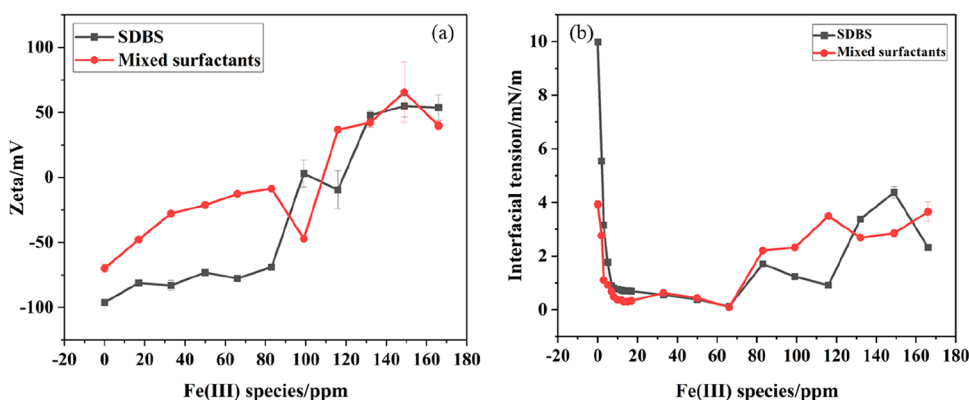


Figure 3. ζ potential (a) and IFT (b) with different Fe(III) species concentrations. The solid lines are guides for the eye.

weakens the electrostatic repulsion force between droplets, resulting in the coalescence of droplets to form an unstable O/W emulsion.^{32,33} Simultaneously, the droplets of the O/W emulsion become larger with an increase in the concentration of Fe(III) species as shown in Figure 4a,c. Therefore, there is a strong correlation between droplet size and ζ potential, which is consistent with the results reported in a previous report.¹⁴

Figure 3b and Figure S2 show the IFT before the phase inversion point and the surface tension of SDBS with different Fe(III) species concentrations at model oil–water and air–solution interfaces, respectively, in which the IFT and surface tension both decrease with an increase in Fe(III) species concentration, indicating the formation of the SDBS–Fe(III) species complex at the interface. This is consistent with previous studies, in which a multivalent cation combines with the polar headgroup of the anionic surfactant to form a surfactant–cation complex, which enhances the adsorption of the surfactant on the interface, resulting in a decrease in IFT or surface tension.^{34,35}

With a further increase in Fe(III) species concentration, a W/O emulsion is obtained due to the more lipophilic SDBS–Fe(III) species complexes being formed because of the increase in ionic strength in the system and the Bancroft rule. In addition to increasing the ionic strength of the aqueous solution, effectively compressing the electric double layer of the polar group of the surfactant and enhancing its adsorption concentration at the interface, the electrolyte can also automatically distribute the surfactant to the oil phase.²⁸ When the partition coefficient of the surfactant in the oil–water two phases is 1, the IFT has a minimum value, while the

partition coefficient deviates from 1 when the electrolyte increases again, resulting in an increased IFT.³⁶ Therefore, the partition coefficient of SDBS in oil–water phases gradually deviates from 1 with an increase in Fe(III) species concentration in this system after reaching the phase inversion point, causing the increased IFT shown in Figure 3b, which is also the reason for the transformation from an O/W emulsion to a W/O emulsion.

The stability of the W/O emulsion was studied by assessing the EI. Figure 5 shows that the Fe(III) species has a great influence on the EI. The EI increases after 4 h in the presence of SDBS or SDBS and EO groups with an increase in Fe(III) species concentration, indicating that the Fe(III) species improves the stability of the W/O emulsion. The W/O emulsion obtained in this paper is more stable than that in an existing experimental result,³⁷ which may be due to the low Fe(III) species concentration added. This is because an increase in ionic strength will make the lipophilic surfactant transition to the oil phase, so as to reduce the adsorption of the surfactant on the interface.²⁸ The absolute value of the ζ potential increases with an increase in Fe(III) species concentration after reaching the phase transition point, as shown in Figure 3a, which indicates that the amount of charge on the droplet surface increases with an increase in Fe(III) species concentration, leading to an increase in electrostatic repulsion between droplets and the formation of a stable W/O emulsion.

The existence of EO groups has a significant effect on the stability of an emulsion. In the presence of EO groups, the O/W emulsion is more unstable (Figure 2b), while the W/O

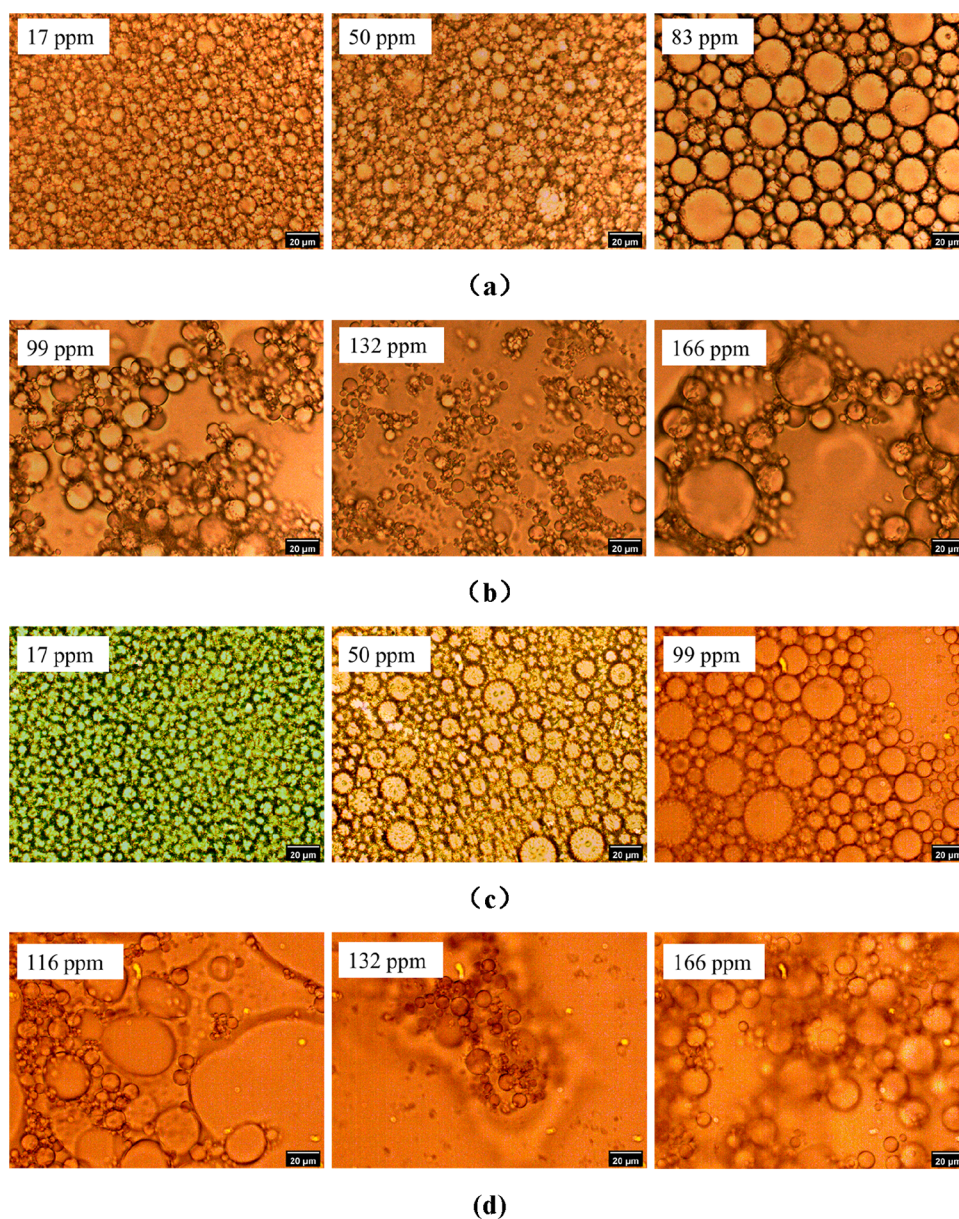


Figure 4. Microscopic morphology of droplets with different Fe(III) species concentrations. The emulsifiers are (a) SDBS, (b) SDBS, (c) mixed surfactants, and (d) mixed surfactants, respectively. The types of mixtures are (a) O/W, (b) W/O, (c) O/W, and (d) W/O, respectively.

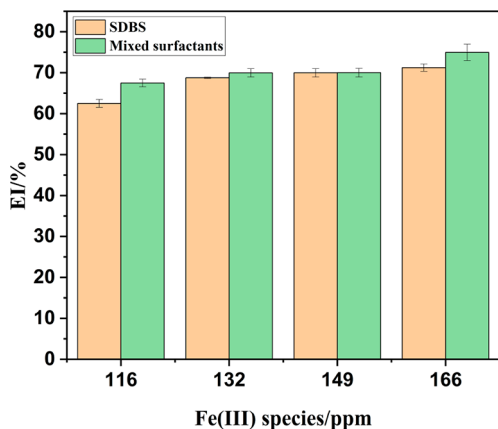


Figure 5. Emulsification indexes (EIs) of the W/O emulsions with an increase in Fe(III) species concentration.

emulsion is more stable (Figure 5). In a mixed system of an anionic surfactant and a nonionic surfactant, on the one hand, the existence of EO groups can reduce the electrostatic repulsion between anionic head groups, and the surfactants are closely arranged at the interface. On the other hand, when multivalent counterions exist, EO groups can hinder the transition of the surfactant at the interface from monolayer to multilayer, and when the concentration of EO groups remains unchanged, there is a greater concentration of multivalent counterions and more adsorption layers.^{38–42} Therefore, we believe that in the O/W emulsion, due to the low concentration of Fe(III) species compared with the former, EO groups play a major role in hindering the formation of a multilayer structure of the surfactant at the interface, resulting in a low strength of the interfacial film. Therefore, compared with the O/W emulsion without EO groups, its stability is poor. In contrast, since the amount of EO groups is fixed, the concentration of Fe(III) species in a W/O emulsion is higher

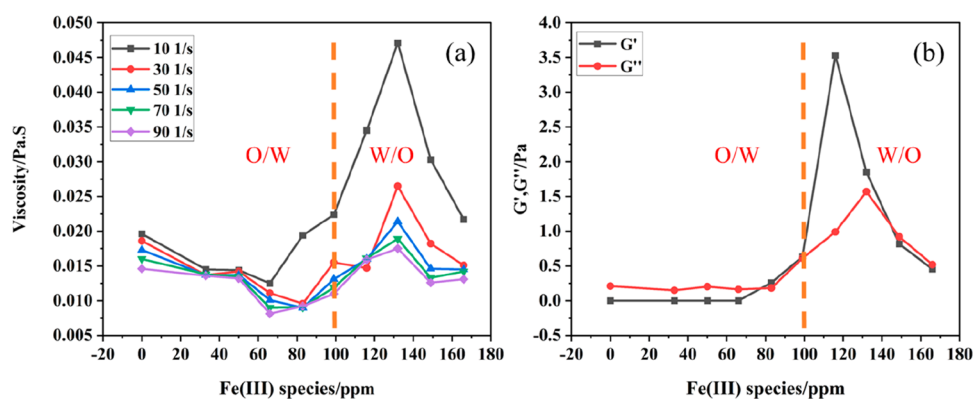


Figure 6. Viscosity (a) and viscoelasticity (b) for water-model oil emulsions with different Fe(III) species concentrations. The dotted line represents the dividing line of emulsion type. The solid lines are guides for the eye.

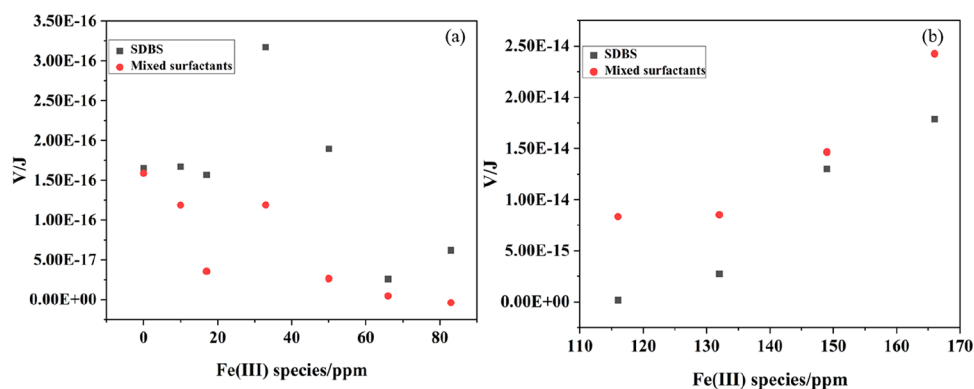


Figure 7. Total potential energies of (a) an O/W emulsion and (b) a W/O emulsion with different Fe(III) species concentrations.

and the inhibiting effect of EO groups is weakened; the former plays a major role, resulting in an increase in the strength of the interfacial film. Therefore, compared with a W/O emulsion without EO groups, its stability is stronger. It is noteworthy that the inhibiting effect of EO groups is also the reason for the higher Fe(III) species concentration required for phase inversion.

2.3. Correlation between Rheology and Model Oil Emulsion Stability. The rheological behaviors of water-model oil emulsions with different Fe(III) species concentrations in the presence of SDBS were investigated in order to better understand the effect of Fe(III) species on the emulsion stability.

Figure 6a reveals the viscosity of the water-model oil emulsions with different Fe(III) species concentrations. The viscosity decreases with an increase in shear rate in all the samples, showing the characteristic of a non-Newtonian fluid and typical shear-thinning.¹⁴ Shear-thinning behavior is a universal behavior in various emulsions, which is considered to be the rearrangement of microstructures arising from the shear stress inside the emulsions.^{43,44} In Figure 6a, the viscosity decreases at the given shear rate with the increase of Fe(III) species concentration in the O/W emulsion, and there is the highest viscosity at 132 ppm in the W/O emulsion system at the given shear rate. The change of viscosity in the presence of Fe(III) species is associated with the droplet size, as shown in Figure 4a,b, in which smaller a droplet size contributes to an increase in the viscosity.⁴³ A decrease in the droplet size results in a decrease in the spacing between droplets, which increases the interaction between droplets, leading to an

increase in the emulsion viscosity. Therefore, for an O/W emulsion, with an increase in Fe(III) species concentration, the droplet size increases, resulting in a decrease of the interaction between droplets, thus reducing the viscosity of the O/W emulsion. For a W/O emulsion, with an increase in Fe(III) species concentration, the droplet size first increases and then decreases, resulting in the interaction between droplets first increasing and then decreasing, so that the viscosity of the W/O emulsion has a maximum value.

The viscoelastic behavior was studied to characterize the emulsion stability in order to understand further the rheological characteristic of the emulsion. The storage modulus (G') represents the extent of energy stored in the emulsions, and the loss modulus (G'') shows the energy loss because of the viscous dissipation. Therefore, the elastic property plays a dominant role in the viscoelastic properties when $G' > G''$ and the viscous property plays an essential role in the viscoelastic properties when $G'' > G'$. Figure 6b shows the viscoelasticity for the water-model oil emulsions with different Fe(III) species concentrations, in which G'' is greater than G' before the phase inversion point, indicating that the viscous property is important in the O/W emulsion. After the phase inversion point, G' is higher than G'' , showing that the elastic property is dominant in the W/O emulsions. In general, a stable emulsion is formed when G' is greater than G'' . Therefore, the addition of Fe(III) species causes a preference to form a stable W/O emulsion rather than an O/W emulsion. The results of the stability of emulsions obtained by rheological measurements agree with the stability experiment results obtained by a bottle test. The result is consistent with the result in a previous study

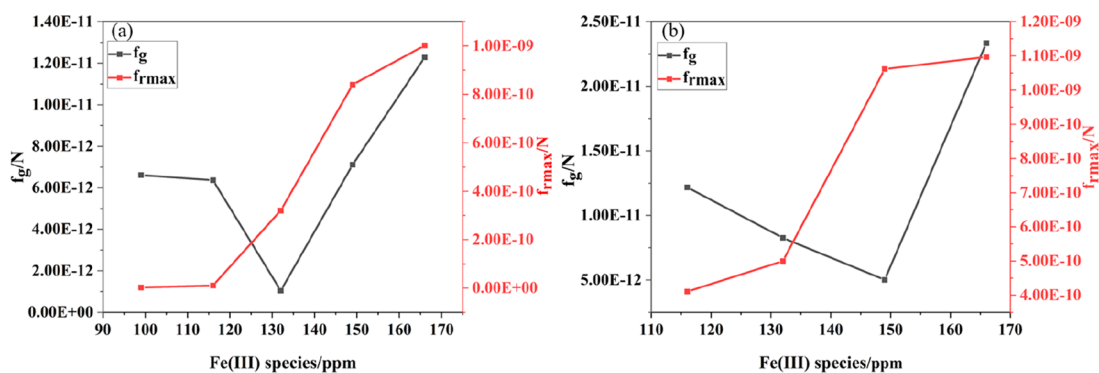


Figure 8. Droplet gravity and the maximum value of electrostatic repulsion between droplets with different Fe(III) species concentrations. The emulsifiers are (a) SDBS and (b) mixed surfactants, respectively. The solid lines are guides for the eye.

that the rheology could predict the stability of emulsions.¹⁴ This phenomenon may be due to the fact that the properties of the emulsion droplets are changed by the adsorption of salt ions on the surfactants layer of the interfacial film, thus resulting in a change in the viscoelasticity of the emulsion.⁴⁵

2.4. Correlation between DLVO Theory and Model Oil Emulsion Stability. DLVO theory describes colloidal stability and explains the charged colloidal solution theory, applying to many colloidal systems. According to DLVO theory, the total potential energy (V) between two droplets is determined by the sum of the van der Waals potential energy and the electrostatic potential energy between colloidal particles.^{46–49} In this study, DLVO theory was used to calculate the interaction energy between two droplets to confirm theoretically the effect of Fe(III) species on the emulsion stability, in which the droplet was assumed to be spherical.⁴⁸ The steric repulsive potential energy coming from the overlap or compression of an adsorption layer on the droplet surface should be considered when $H_0 < 2\delta$ (δ represents the thickness of adsorption layer on the droplet surface), while the interaction between two droplets depends on the van der Waals potential energy and electrostatic potential energy when $H_0 > 2\delta$.^{50–52} It was assumed that the thickness of the adsorption layer δ is the length of the hydrophobic tail chain of the surfactant adsorbed on the droplet surface. It can be seen from Figure 4 that H_0 is much larger than the length of the hydrophobic tail chain of SDBS; thus, the van der Waals potential energy and electrostatic potential energy were only considered when the total potential energy was calculated.

Figure 7 depicts the calculation results of the total potential energy between two droplets based on DLVO theory. The greater the total potential energy of the emulsions, the higher the potential barrier to be crossed for droplet coalescence based on DLVO theory, thus enhancing the emulsion stability. In Figure 7a, with increasing Fe(III) species concentrations, the total potential energy of the O/W emulsion decreases, and compared with the total potential energy in the presence of EO groups, a higher total potential energy exists in the O/W emulsion without EO groups. Therefore, the addition of Fe(III) species is unfavorable for forming a stable O/W emulsion, in which the O/W emulsion stabilized by SDBS is more stable than that stabilized by SDBS and EO groups. In Figure 7b, the total potential energy of the W/O emulsion increases with increasing Fe(III) species concentration, and the total potential energy in the presence of the EO groups is greater. Therefore, the presence of Fe(III) species improves

the stability of the W/O emulsion, and the stability of the W/O emulsion with EO groups is higher.

Therefore, these results obtained by DLVO theory calculations are consistent with the stability experiment results obtained by the bottle test, which indicates that DLVO theory can well explain the effect of Fe(III) species on the stability of the emulsion stabilized by SDBS with and without EO groups.

However, the droplet in the W/O emulsion usually has a greater density; thus, the gravity of the droplet must also be considered in addition to the total potential energy. In addition, the maximum value of electrostatic repulsion produced by the charge on the droplet surface is also considered. The stability of the W/O emulsion is affected by the relative value between gravity and maximum value of electrostatic repulsion. The gravity of a droplet with particle radius a is obtained by eq 1

$$f_g = \frac{4\pi a^3 g(\rho_1 - \rho_2)}{3} \quad (1)$$

where g is the gravitational acceleration and the densities of the droplet and dispersion medium are represented as ρ_1 and ρ_2 , respectively. f_g is the factor of the W/O emulsion sedimentation, and the repulsion force f_r is against f_g . The maximum value $f_{r,max}$ of f_r is obtained by eq 2

$$f_{r,max} = \frac{\epsilon \psi_0^2 (1 + 2\kappa a)}{4} \quad (2)$$

where ϵ is the dielectric constant of the continuous phase, ψ_0 is the interfacial potential, and κ is the Debye parameter.

Figure 8 shows the relationship between the gravity of the droplet and the maximum value of repulsion between droplets with the existence of Fe(III) species in the W/O emulsion. The gravity decreases first and then increases with an increase in Fe(III) species concentration, in which the lowest value appears at the smallest droplet size, indicating that a large droplet favors an increase in the gravity. However, the maximum value of electrostatic repulsion increases and is greater than the gravity with an increase in Fe(III) species concentration. Therefore, the electrostatic repulsion plays a dominant role in the W/O emulsion. The electrostatic repulsion can hinder the small droplets to form large droplets, avoiding the aggregation and sedimentation of the droplets. Therefore, the addition of Fe(III) species is helpful to an increase in W/O emulsion stability. Compared to the maximum value of electrostatic repulsion in Figure 8a, the maximum value of electrostatic repulsion is greater in Figure

8b. Therefore, the addition of EO groups improves the stability of the W/O emulsion with different Fe(III) species concentrations. More importantly, these outcomes obtained from Figure 8 are in accord with the stability experiment results.

2.5. Effect of Fe(III) Species Concentration on the Crude Oil Emulsion Stability. In order to further verify that the Fe(III) species also has an effect on the stability of the crude oil emulsion, the stability of the W/O crude oil emulsion with different Fe(III) species concentrations were tested, as shown in Figure 9.

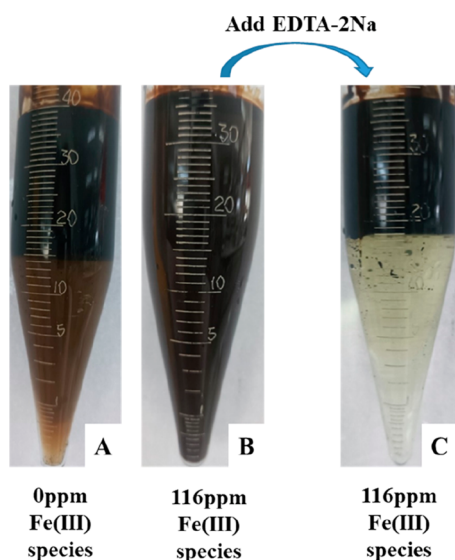


Figure 9. Images of crude oil–water separation of W/O crude oil emulsions (A–C) after 4 h.

In Figure 9, an apparent phase separation appears for emulsion A in the absence of Fe(III) species, while there is no macroscopic phase separation for the Fe(III)-species-rich emulsion B, indicating that the addition of Fe(III) species can make the W/O crude oil emulsion more stable.

In order to further study the effect of Fe(III) species concentration on the stability of a W/O crude oil emulsion, EDTA-2Na, a common metal ion chelating agent, was added to the system C according to the ratio $n_{\text{Fe(III) species}}/n_{\text{EDTA-2Na}} = 1$. Compared with the emulsion B without the chelating agent, the volume of precipitated water for emulsion C increases and is clear. This again confirms that the Fe(III) species favors the stability of W/O crude oil emulsion. That is, the Fe(III) species is favorable to the stability of the W/O emulsion in both the crude oil system and model oil system.

3. CONCLUSIONS

The effects of Fe(III) species on the stability, microscopic morphology of droplets, interfacial properties, and rheology of the water-model oil emulsions were studied by changing the Fe(III) species concentration in the presence of SDBS. The

interaction energy between two droplets was calculated based on DLVO theory to theoretically confirm the effect of Fe(III) species on the stability of the water-model oil emulsion in the presence of SDBS. In addition, the effect of EO groups on the model oil emulsion stability in the presence of SDBS and Fe(III) species was also studied. The effect of Fe(III) species on the stability of the W/O crude oil emulsion was also explored.

The experimental results show that the addition of Fe(III) species is unfavorable for the stability of the O/W model oil emulsion in the presence of SDBS, in which the O/W model oil emulsion is reversed to a W/O model oil emulsion with the addition of 99 ppm of Fe(III) species and the droplet size increases with an increase in Fe(III) species concentration. With an increase in Fe(III) species concentration, a stable W/O model oil emulsion and W/O crude oil emulsion are obtained. The rheological results demonstrate that modifying the Fe(III) species concentration has a significant effect on the viscosity and the viscoelastic behaviors of the water-model oil emulsion, in which a higher viscosity in the W/O model oil emulsion than that in the O/W model oil emulsion and the viscous property and elastic property are displayed in the O/W model oil emulsion and W/O model oil emulsion, respectively. The potential energy of the O/W model oil emulsion decreases and that of W/O model oil emulsion increases with an increase in Fe(III) species concentration. Moreover, the maximum value of electrostatic repulsion between droplets in the W/O model oil emulsion increases with increasing Fe(III) species concentration. Otherwise, the existence of EO groups has a great impact on the stability of the water-model oil emulsion. The addition of EO groups makes the phase inversion point appear later than that without EO groups, forming a more stable W/O model oil emulsion and a more unstable O/W model oil emulsion. The total potential energy of the O/W model oil emulsion is lower; however, the total potential energy and the maximum value of electrostatic repulsion are higher in the W/O model oil emulsion.

The research results can provide great assistance for a comprehensive understanding of the effects of Fe(III) species on the stability of an emulsion emulsified by an anionic sulfonate surfactant and be of great significance to improve the oil displacement efficiency of an emulsion emulsified by an anionic sulfonate surfactant.

4. EXPERIMENTAL SECTION

4.1. Materials. Analytical grade (>99.0% purity) sodium dodecyl benzenesulfonate (SDBS) and chemical grade (>97.0% purity) FeCl_3 were obtained from Sinopharm Chemical Reagent Co. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) (analytical grade, >99.0% purity) was purchased from Jinan reagent factory. Kerosene was purchased from Tianjin Damao chemical reagent factory. Crude oil-1, crude oil-2, and OP-10 were obtained from the Shengli oilfield. The basic physical properties and component contents of

Table 1. Basic Physical Properties and Component Content of Crude Oil

sample	density (25 °C) (g/cm ³)	viscosity (50 °C) (mPa s)	acid value (mg KOH/g)	asphaltene content (wt %)	total content of resin, saturate and aromatic (wt %)
crude oil-1	0.98	5091	0.954	6.98	93.02
crude oil-2	0.93	322.2	1.839	0.98	99.02

crude oils are shown in Table 1, and the infrared spectrum of the OP-10 is shown in Figure S3.

4.2. Emulsion Preparation. The water-model oil emulsions with and without Fe(III) species were prepared by using a kerosene solution containing 1 wt % crude oil-1 as the oil phase. Table S1 gives the recipe of water-model oil emulsions with different SDBS concentrations without Fe(III) species. Tables S2 and S3 show the formulation of water-model oil emulsions with and without OP-10, respectively. The pH values of aqueous solution measured by a pH meter (PHS-3C, Shanghai INESA Scientific Instrument Co., Ltd.) are shown in Tables S4 and S5. Distribution fractions of the Fe(III) species in aqueous solution are shown in Tables S6 and S7, in which the main form of Fe(III) in the aqueous phase is $\text{Fe}(\text{OH})^{2+}$, followed by Fe^{3+} . In the mixed surfactant solution, the concentration of polyether surfactant in the mixed surfactant is 16.43 ppm, and the total concentration of the mixed surfactant is 3016.43 ppm. The sequence of preparation was first keeping the water phase and oil phase for 20 min in a water bath at 50 °C, respectively, and then mixing the two phases for 20 min with a homogenizer (Polytron pt2500e, Kinematica, Switzerland) at a speed of 10000 rpm. The emulsion types were created by using a drop dilution method.

The W/O crude oil emulsions with and without Fe(III) species were prepared by mixing 0.3 wt % SDBS aqueous solution and crude oil-2 at 50 °C using a high-speed stirrer (GJ-3S) at a rotating speed of 3000 rpm for 20 min, in which the oil–water mass ratio was 1:1. EDTA-2Na was used as a chelating agent to partially shield Fe(III) species.

4.3. Emulsion Stability. The stability of the water-model oil emulsion was characterized by a bottle test to show the degree of phase separation in a water bath at a constant temperature at 50 °C for 4 h. The emulsion stability was characterized by EI,^{24,53} which was calculated according to eq 3. The prepared emulsion was poured into a 50 mL graduated glass tube, the mixture total volume was recorded as V_0 by reading, and the volume of the emulsion layer was recorded as V_E by reading when the emulsion was stratified after standing for 4 h.

$$\text{EI} (\%) = \frac{V_E}{V_0} \times 100 \quad (3)$$

The emulsification index (EI) is the percent of the emulsion layer volume to the total volume of the mixture.

4.4. Microscopic Morphology. A droplet of the prepared emulsion was placed in the center of a glass slide and covered with a cover glass to avoid bubbles. The droplet slides were placed on an optical microscope (BA310-T) stage to observe the microscopic morphology of the emulsion with 400× magnification.

4.5. ζ Potential and Droplet Size. The droplet size and ζ potential were both measured by a ζ potential and nanoparticle size analyzer (NanoBrook 90Plus PALS, Brookhaven Instruments, USA). The droplet size was tested based on the principle of the dynamic light scattering (DLS) technique at a scattering angle of 90°. The ζ potential was determined by using the phase analysis light scattering (PALS) technique.

4.6. Interfacial Tension and Surface Tension Measurements. The IFT of the water–oil interface with and without Fe(III) species was determined using a TX-500C spinning drop tensiometer (Shanghai Zhongchen digital technology equipment company). The procedure used a

syringe to inject an SDBS solution with and without Fe(III) species into the quartz tube and then to inject a drop of kerosene into it, and then system was rotated at a speed of 6000 rpm. The IFT was calculated when the oil droplet was no longer elongated. The surface tensions of the SDBS aqueous solution with and without Fe(III) species were determined using a JK99C automatic tensiometer (Shanghai Zhongchen digital technology equipment company). For each sample, the surface tension value and the IFT value were both the average of three measurements to reduce the experimental error.

4.7. Rheological Measurements. The rheological characteristics and the viscoelasticities of the water-model oil emulsions were measured using a MCR302 rheometer purchased from Thermo Haake company. The viscosity of the emulsion was obtained when the shear rates were 1–100 rad/s and the test point was 20. The elastic modulus (G') and viscous modulus (G'') of the emulsion were obtained at a fixed frequency of 10 rad/s.

4.8. Derjaguin–Landau–Verwey–Overbeek (DLVO) Theory. DLVO theory is very useful for understanding colloidal stability, especially for evaluating the stability of an emulsion.^{54–59} The effect of Fe(III) species on the stability of the emulsion was estimated based on DLVO theory.

The van der Waals potential energy can be expressed by

$$V_A = -\frac{A_{101}}{12} \frac{a}{H_0} \quad (4)$$

where V_A is the van der Waals potential energy, a is the droplet radius, and H_0 is the surface shortest distance between two droplets. Equation 4 is applicable to water-in-oil (W/O) and oil-in-water (O/W) emulsions.

$$A_{101} = (A_{11}^{1/2} - A_{00}^{1/2})^2 \quad (5)$$

where A_{101} is the Hamaker constant of a dispersed phase immersed in a dispersed medium, A_{11} is the Hamaker constant of the dispersed phase, and A_{00} is the Hamaker constant of the dispersed medium.

$$A_{11 \text{ or } 00} = \left(\frac{\pi \rho N_A}{M} \right)^2 \frac{3h\nu\alpha^2}{4} \quad (6)$$

where h is Planck's constant, α is the polarizability, ν is the vibration frequency, N_A is Avogadro's constant, ρ is the density of the dispersed phase or dispersed medium, and M is the molecular mass of the dispersed phase or dispersed medium.

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4\pi N_A \alpha}{3} \quad (7)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{e^2}{\alpha m_e}} \quad (8)$$

where n is the refractive index of the dispersed phase or dispersed medium, for nonpolar molecules, the dielectric constant is equal to the square of the refractive index, e is the electronic charge, and m_e is the electronic mass.

The electrostatic potential energy can be given by

$$V_R = \frac{64\pi a n_0 k T \nu_0^2}{\kappa^2} e^{(-\kappa H_0)} \quad (9)$$

where V_R is the electrostatic potential energy, T is the absolute temperature, k is Boltzmann's constant, n_0 and ν_0 are obtained by eqs 10 and 11, respectively, and κ is the Debye parameter

which is calculated by eq 12. Equation 9 is applicable to the O/W emulsion.

$$n_0 = cN_A \quad (10)$$

where c is the electrolyte concentration.

$$\nu_0 = \frac{e^{(ze\psi_0/2kT)} - 1}{e^{(ze\psi_0/2kT)} + 1} \quad (11)$$

where z is the valence number of ions and ψ_0 is the potential of the electrical double layer.

$$\kappa = \left(\frac{e^2 N_A \sum_i c_i z_i^2}{\epsilon k T} \right)^{1/2} \quad (12)$$

where c_i is the concentration of the ion at the ψ potential and ϵ is the dielectric constant.

$$V_R = \frac{\epsilon a^2 \psi_0^2}{H} \quad (13)$$

where H is the center distance between two spheres. Equation 13 is applicable to a W/O emulsion.

The total potential energy V can be obtained by

$$V = V_A + V_R \quad (14)$$

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03984>.

Photo of the solubility of the SDBS-Fe(III) species complex in kerosene and deionized water, variation of surface tension of an SDBS aqueous solution with Fe(III) species concentration, infrared spectrum of OP-10, formulation for water-model oil emulsions with different SDBS concentrations without Fe(III) species, formulation for water-model oil emulsions containing Fe(III) species and OP-10, formulation for water-model oil emulsions containing Fe(III) species, determinations of some constants in DLVO theory, partial oil–water separation pictures of a model oil emulsion on standing for different times, pH values of the aqueous phase with mixed surfactants, pH values of the aqueous phase with SDBS, distribution fraction of the Fe(III) species in aqueous solution with mixed surfactants, and distribution fraction of the Fe(III) species in aqueous solution with SDBS (PDF)

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Notes

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